

CLAIMS

1. A microporous membrane produced by cooling a solution comprising a vinylidene fluoride homopolymer or copolymer having a weight average molecular weight of 1×10^5 or more and a solvent therefor, to form a two-phase gel, said microporous membrane comprising a polymer phase comprising said vinylidene fluoride homopolymer or copolymer, and intercommunicating voids which have an average pore size measured by the half-dry method of 0.005 to 5 μm and extend from one side of the membrane to the other side, and said microporous membrane having the percolation structure defined in (A) below, as its internal structure:

(A) a structure in which the polymer phase forms an isotropic network structure by three-dimensional branching in arbitrary directions, the voids are formed within an area surrounded by said polymer phase of the network structure and intercommunicate with one another, and the ratio of the maximum pore size measured by the bubble point method to the average pore size measured by the half-dry method is 2.0 or less.

2. The microporous membrane according to claim 1, wherein the average pore size measured by scanning electron microscopy of the surface layer on at least one side of the microporous membrane is the same as or larger than the average pore size measured by scanning electron microscopy of the internal structure.

3. The microporous membrane according to claim 1,

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wherein the average pore size measured by scanning electron microscopy of the surface layer on at least one side of the microporous membrane is smaller than the average pore size measured by scanning electron microscopy of the internal structure.

4. The microporous membrane according to claim 1, wherein the average pore size measured by the half-dry method is 0.005 to 0.1 μm .

5. A process for producing a microporous membrane which comprises using a vinylidene fluoride homopolymer or copolymer having a weight average molecular weight of 1×10^5 or more and a solvent capable of forming a microporous membrane having a percolation structure as defined in (B) below, in a weight ratio of 10 : 90 to 60 : 40; dissolving said vinylidene fluoride homopolymer or copolymer in said solvent at a dissolution temperature T_s at which the percolation structure can be formed and which satisfies the condition described in (C) below; extruding the resulting solution with an extruder; cooling the extruded solution to form a gel-like shaped product composed of a two-phase gel; and then subjecting the shaped product to any treatment selected from the group consisting of the following treatments i), ii) and iii):

i) removing the solvent by use of a volatile liquid without stretching the shaped product,

ii) stretching the shaped product with a stretching residual strain of 100% or less and then

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removing the solvent by use of a volatile liquid,

iii) removing the solvent by use of a volatile liquid, followed by stretching with a stretching residual strain of 100% or less;

(B) said solvent capable of forming a microporous membrane having the percolation structure being defined as such a solvent that, for solutions of the vinylidene fluoride homopolymer or copolymer with a weight average molecular weight of 1×10^5 or more having concentrations in a range of 10 to 60 wt%, when dissolution temperature T_s is plotted as abscissa at regular intervals of 5°C , starting from $T_s = 100^\circ\text{C}$, and the breaking extension TL of a membrane produced from the solution having each dissolution temperature is plotted as ordinate, a dissolution temperature at which $-(TL_{s+5} - TL_s) / \{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein TL_{s+5} is a TL value at $T_s + 5^\circ\text{C}$ and TL_s is a TL value at T_s) becomes maximum is taken as $T_s \text{ max}$, and a temperature 2.5°C higher than $T_s \text{ max}$ ($T_s \text{ max} + 2.5^\circ\text{C}$) is taken as T_u ; on the other hand, when T_s is plotted as abscissa and the porosity P of the membrane as ordinate in the same manner as above, a dissolution temperature at which $(P_{s+5} - P_s) / \{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein P_{s+5} is a P value at $T_s + 5^\circ\text{C}$ and P_s is a P value at T_s) becomes maximum is taken as $T's \text{ max}$, and a temperature 2.5°C higher than $T's \text{ max}$ ($T's \text{ max} + 2.5^\circ\text{C}$) is taken as T_l ; and at least one solution having a concentration in the above range of the concentration of the vinylidene fluoride homopolymer

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or copolymer has both T_l and T_u in such a way that $(T_u - T_l) > 0$;

(C) $T_l \leq T_s \leq T_u$.

6. The process for producing a microporous membrane according to claim 5, wherein a liquid cooling medium is at least one medium selected from solvents capable of forming a microporous membrane having the percolation structure.

7. The process for producing a microporous membrane according to claim 6, wherein the liquid cooling medium is at least one member selected from the group consisting of phthalic acid esters, benzoic acid esters, sebacic acid esters, adipic acid esters, trimellitic acid esters, phosphoric esters and ketones.

8. A gel-like shaped product composed of a two-phase gel which is obtained by using a vinylidene fluoride homopolymer or copolymer having a weight average molecular weight of 1×10^5 or more and a solvent capable of forming a microporous membrane having the percolation structure which is defined in (B) below, in a weight ratio of 10 : 90 to 60 : 40; dissolving said vinylidene fluoride homopolymer or copolymer in said solvent at a dissolution temperature T_s at which the percolation structure can be formed and which satisfies the condition described in (C) below; extruding the resulting solution with an extruder; and then cooling the extruded solution;

(B) said solvent capable of forming a

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microporous membrane having the percolation structure being defined as such a solvent that, for solutions of the vinylidene fluoride homopolymer or copolymer having any concentrations in a range of 10 to 60 wt%, when dissolution temperature T_s is plotted as abscissa at regular intervals of 5°C , starting from $T_s = 100^\circ\text{C}$, and the breaking extension TL of a membrane produced from the solution having each dissolution temperature is plotted as ordinate, a dissolution temperature at which $-(TL_{s+5} - TL_s) / \{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein TL_{s+5} is a TL value at $T_s + 5^\circ\text{C}$ and TL_s is a TL value at T_s) becomes maximum is taken as $T_s \text{ max}$, and a temperature 2.5°C higher than $T_s \text{ max}$ ($T_s \text{ max} + 2.5^\circ\text{C}$) is taken as T_u ; on the other hand, when T_s is plotted as abscissa and the porosity P of the membrane as ordinate in the same manner as above, a dissolution temperature at which $(P_{s+5} - P_s) / \{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein P_{s+5} is a P value at $T_s + 5^\circ\text{C}$ and P_s is a P value at T_s) becomes maximum is taken as $T's \text{ max}$, and a temperature 2.5°C higher than $T's \text{ max}$ ($T's \text{ max} + 2.5^\circ\text{C}$) is taken as T_l ; and at least one solution having a concentration in the above range of the concentration of the vinylidene fluoride homopolymer or copolymer has both T_l and T_u in such a way that $(T_u - T_l) > 0$;

$$(C) \quad T_l \leq T_s \leq T_u.$$

9. A process for producing a microporous membrane which comprises using a vinylidene fluoride homopolymer or copolymer having a weight average molecular weight of

1 x 10⁵ or more and a mixture of a solvent capable of forming a microporous membrane having a percolation structure which is defined in (B) below and a thermoplastic resin miscible with said vinylidene fluoride homopolymer or copolymer, in a weight ratio of 10 : 90 to 60 : 40; dissolving the vinylidene fluoride homopolymer or copolymer and the thermoplastic resin miscible therewith in the said solvent at a dissolution temperature Ts at which the percolation structure can be formed and which satisfies the condition described in (C) below, under such conditions that the total amount of said vinylidene fluoride homopolymer or copolymer and the thermoplastic resin miscible therewith is 60 wt% or less based on the weight of the resulting solution consisting of said vinylidene fluoride homopolymer or copolymer, said thermoplastic resin and said solvent, and the weight ratio of said vinylidene fluoride homopolymer or copolymer to the thermoplastic resin miscible therewith is 40 : 60 to 90 : 10; then extruding the solution with an extruder; cooling the extruded solution to form a gel-like shaped product composed of a two-phase gel; and then subjecting the shaped product to any treatment selected from the group consisting of the following treatments iv), v) and vi):

iv) removing the solvent and the thermoplastic resin miscible with the vinylidene fluoride homopolymer or copolymer by use of a volatile liquid without stretching the shaped product;

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v) stretching the shaped product with a stretching residual strain of 100% or less, and then removing the solvent and the thermoplastic resin miscible with the vinylidene fluoride homopolymer or copolymer by use of a volatile liquid; and

vi) removing the solvent and the thermoplastic resin miscible with the vinylidene fluoride homopolymer or copolymer by use of a volatile liquid, followed by stretching with a stretching residual strain of 100% or less;

(B) said solvent capable of forming a microporous membrane having the percolation structure being defined as such a solvent that, for solutions of the vinylidene fluoride homopolymer or copolymer with a weight average molecular weight of 1×10^5 or more having any concentrations in a range of 10 to 60 wt%, when dissolution temperature T_s is plotted as abscissa at regular intervals of 5°C , starting from $T_s = 100^\circ\text{C}$, and the breaking extension TL of a membrane produced from the solution having each dissolution temperature is plotted as ordinate, a dissolution temperature at which $-(TL_{s+5} - TL_s) / \{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein TL_{s+5} is a TL value at $T_s + 5^\circ\text{C}$ and TL_s is a TL value at T_s) becomes maximum is taken as $T_s \text{ max}$, and a temperature 2.5°C higher than $T_s \text{ max}$ ($T_s \text{ max} + 2.5^\circ\text{C}$) is taken as T_u ; on the other hand, when T_s is plotted as abscissa and the porosity P of the membrane as ordinate in the same manner as above, a dissolution temperature at which (P_{s+5}

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- P_s) / $\{(T_s + 5^\circ\text{C}) - T_s\}$ (wherein P_{s+5} is a P value at $T_s + 5^\circ\text{C}$ and P_s is a P value at T_s) becomes maximum is taken as $T's \text{ max}$, and a temperature 2.5°C higher than $T's \text{ max}$ ($T's \text{ max} + 2.5^\circ\text{C}$) is taken as T_l ; and at least one solution having a concentration in the above range of the concentration of the vinylidene fluoride homopolymer or copolymer has both T_l and T_u in such a way that $(T_u - T_l) > 0$;

(C) $T_l \leq T_s \leq T_u$.

10. The process for producing a microporous membrane according to claim 5 or 9, wherein the solvent capable of forming a microporous membrane having the percolation structure which is defined in (B) is at least one member selected from the group consisting of phthalic acid esters, benzoic acid esters, sebacic acid esters, adipic acid esters, trimellitic acid esters, phosphoric esters and ketones.

11. A process for producing a microporous membrane which comprises using a vinylidene fluoride homopolymer or copolymer having a weight average molecular weight of 1×10^5 or more and a solvent capable of permitting observation of planar liquid-liquid interface which is defined in (D) below, in a weight ratio of 10 : 90 to 60 : 40; uniformly dissolving the vinylidene fluoride homopolymer or copolymer in said solvent to obtain a one-phase solution at a dissolution temperature T_s 10°C or more higher than the cloud point temperature determined by a standing method; extruding the resulting

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solution with an extruder; cooling the extruded solution to form a gel-like shaped product composed of a two-phase gel; and then subjecting the shaped product to any treatment selected from the group consisting of the following treatments vii), viii) and ix):

vii) removing the solvent by use of a volatile liquid without stretching the shaped product;

viii) stretching the shaped product with a stretching residual strain of 100% or less, and then removing the solvent by use of a volatile liquid; and

ix) removing the solvent by use of a volatile liquid, followed by stretching with a stretching residual strain of 100% or less;

(D) a solvent which makes it possible to observe the planar liquid-liquid interface between a phase rich in the vinylidene fluoride homopolymer or copolymer and a phase lean in the vinylidene fluoride homopolymer or copolymer by a standing method comprising lowering the temperature of a solution prepared by uniform one-phase dissolution of the vinylidene fluoride homopolymer or copolymer in the solvent to any concentration in a range of 10 to 60 wt%, to any observation temperature which is not lower than the crystallization temperature and is in a two-phase region, and allowing the solution to stand.

12. A process for producing a microporous membrane according to any one of claims 5, 9 and 11, wherein the solution extruded with the extruder is cooled with at

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least one member selected from the group consisting of liquid cooling media, air and rolls.

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